Verification of Translation

I, Shuji Yoshizaki, hereby verify that I am familiar with Japanese and English. The attachment is a true English translation of Japanese Patent Application No. Hei 11-019745, filed in Japan on January 28, 1999.

Shuji Yoshizaki

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Date

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[List of Attached Documents]

[Document Name]	Description 1
[Document Name]	Abstract 1
[Necessity of Proof]	Needed

[Document Name] Description

[Title of the Invention] POLYMER, PROCESS FOR PRODUCING THE POLYMER AND CURABLE COMPOSITION CONTAINING THE POLYMER

[Scope of Claims for Patent]

[Claim 1] A production method of a polymer having a functional group at a terminus

which comprises adding a compound (I) having an internal olefin during or after completion of polymerization in living radical polymerization.

[Claim 2] The production method according to Claim 1,

wherein the functional group to be introduced into a terminus is a hydroxyl, amino, epoxy, carboxyl, ester, ether, amido, silyl or terminal or internal alkenyl group.

[Claim 3] The production method according to Claim 1 or 2,

wherein the internal olefin in the compound (I) is a cyclic olefin.

[Claim 4] The production method according to any of Claims 1 to 3,

wherein the functional group to be introduced into a terminus is a terminal or internal alkenyl group.

[Claim 5] The production method according to Claim 4,

wherein the compound (I) is 4-vinylcyclohexene or 1,5-cyclooctadiene.

[Claim 6] The production method according to any of Claims 1 to 5,

wherein the living radical polymerization is carried out in the manner of atom transfer radical polymerization.

[Claim 7] The production method of a polymer according to Claim 6,

wherein a metal complex to be used as a catalyst is copper, nickel, ruthenium or iron.

[Claim 8] The production method according to Claim 7,

wherein the metal complex to be used as a catalyst is copper.

[Claim 9] The production method according to any of Claims 6

to 8,

wherein an initiator is an organic halide having a functional group or a halosulfonyl compound having a functional group.

[Claim 10] The production method according to any of Claims 6 to 9,

wherein the initiator is a polyfunctional initiator.

[Claim 11] A vinyl polymer having a functional group at a terminus

which is obtainable by the methods according to Claims 1 to 10.

[Claim 12] The polymer according to Claim 11,

wherein the vinyl polymer is a (meth)acrylate polymer.

[Claim 13] The polymer according to Claim 12,

wherein the vinyl polymer is an acrylate ester polymer.

[Claim 14] The polymer according to Claim 13,

wherein the vinyl polymer is a butyl acrylate polymer.

[Claim 15] The polymer according to any of Claims 11 to 15

which has a number average molecular weight of 500 to 100,000.

[Claim 16] The polymer according to any of Claims 11 to 16

which has a weight average molecular weight (Mw)/number average molecular weight (Mn) ratio (Mw/Mn) of less than 1.8 as determined by gel permeation chromatography.

[Claim 17] A polymer having a crosslinking silyl group at a terminus

which is produced by reacting a polymer, which has an alkenyl group at a terminus and is produced in each Claim, with a hydrosilane compound which has a crosslinking silyl group having a silicon-hydrogen bond.

[Claim 18] A polymer having a crosslinking silyl group at a terminus

which is produced by reacting a polymer, which has a hydroxyl or amino group at a terminus and is producible in each Claim, with a compound having a group capable of reacting with

a hydroxyl group, and a crosslinking silyl group.

[Claim 19] A curable composition comprising:

(A) a polymer, which has an alkenyl group at a terminus and is producible in each Claim,

and (B) a compound having at least two hydrosilyl groups

as essential components.

[Claim 20] A curable composition comprising:

(A) a polymer, which has a hydroxyl or amino group at a terminus and is producible in each Claim,

and (B) a compound having at least two functional groups capable of reacting with a hydroxyl or amino group

as essential components.

[Claim 21] The curable composition according to Claim 20, wherein the component (B) is a polyisocyanate.

[Claim 22] A curable composition comprising:

a polymer having a crosslinking silyl group at a terminus which is produced in each Claim as a main component.

[Claim 23] A curable composition comprising:

a polymer, which has an epoxy group at a terminus and is producible in each Claim,

and (B) a curing agent for epoxy resins

as essential components.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a vinyl polymer having a functional group at a molecular terminus, a production method of the same and a curable composition containing said polymer.

[0002]

[Prior Art]

Polymers having a functional group at each of a plurality of termini are known to crosslink by themselves or when combined with an appropriate curing agent and thereby give cured products excellent in heat resistance, durability, etc. Alkenyl-, hydroxyl- or crosslinking silyl-terminated polymers are

typical examples. Alkenyl-terminated polymers are cured by crosslinking with a hydrosilyl group-containing compound as a curing agent or when subjected to photochemical reaction. Hydroxyl-terminated polymers, when reacted with a polyisocyanate, are cured under formation of urethane crosslinks. Crosslinking silyl-terminated polymers absorb moisture and give cured products in the presence of an appropriate condensation catalyst.

[0003]

As examples of the main chain skeleton of such alkenyl-, hydroxyl- or crosslinking silyl-terminated polymers, there may be mentioned polyether type polymers such as polyethylene oxide, polypropylene oxide and polytetramethylene oxide, hydrocarbon type polymers such as polybutadiene, polyisoprene, polychloroprene, polyisobutylene, and hydrogenation products derived therefrom, polyester type polymers such as polyethylene terephthalate, polybutylene terephthalate and polycaprolactone and so forth. They are used in various fields of application according to the main chain skeleton and mode of crosslinking thereof.

[0004]

[Subject which the Invention is to Solve]

Unlike those polymers obtainable by ionic polymerization or polycondensation, those functional group-terminated vinyl polymers which are obtainable by radical polymerization have scarcely been put to practical use. Among the vinyl polymers, (meth)acrylic polymers have those characteristics, such as high weathering resistance and transparency, among others, which cannot be attainable with the polyether type polymers, hydrocarbon type polymers and polyester type polymers mentioned above. Among them, those having an alkenyl or crosslinking silyl group on their side chain(s) are utilized in highly weathering resistant coatings. In the case of acrylic polymers, on the other hand, it is not easy to control the polymerization thereof because of side reactions involved therein; it is very

difficult, for instance, to introduce a functional group into a terminus thereof.

[0005]

If vinyl polymers having an alkenyl group, at a molecular chain terminus can be obtained in a simple and easy manner, cured products superior in cured product physical properties as compared with those having a crosslinking group on a side chain or chains will possibly be obtained. Thus, a number of researchers have so far searched for a method of producing them. It is not easy, however, to produce them industrially.

[0006]

Japanese Kokai Publication Hei-05-255415 discloses a method of synthesizing (meth)acrylic polymers having an alkenyl group at both termini which uses an alkenyl-containing disulfide as a chain transfer agent. Japanese Kokai Publication Hei-05-262808 discloses a method of synthesizing (meth)acrylic polymers having an alkenyl group at both termini which uses a hydroxyl-containing disulfide to thereby synthesize (meth)acrylic polymers having a hydroxyl group at both termini and then further utilizes the reactivity of the hydroxyl group. By these methods, however, it is not easy to realize the alkenyl group introduction into both termini with certainty. Further, for attaining terminal functional group introduction with certainty, it is necessary to use a chain transfer agent in large amounts. This is a problem from the production process viewpoint.

[0007]

Accordingly, it is an object of the present invention to make the production of polymers having a functional group at a terminus more practical by introducing the functional group into a terminus by using an internal olefin compound which is relatively readily available. By the present invention, it is possible to produce a polymer having a functional group at a terminus with advantage, thus the present invention is industrially very useful.

[0008]

[Means for Solving the Problems]

It is known that unactivated olefins, such as α-olefins, will not polymerize in radical polymerization in general. This is also the case with living radical polymerization, which has recently been studied widely.

[0009]

The inventors have made intensive investigations independently and, as a result, found that when an unactivated (low in polymerizability) olefin is added to a living radical polymerization system, approximately only one molecule adds to each growing terminus. By utilizing this, they have now invented a production method of a polymer having various terminal functional groups.

[0010]

According to the present invention, it is possible to terminally introduce a functional group by using an internal olefin compound whose commercial availability is growing.

[0011]

Thus, a first aspect of the present patent is a production method of a polymer having a functional group at a terminus which comprises adding a compound (I) having an internal olefin either during or after completion of polymerization in living radical polymerization. Additionally, the "internal olefin" according to the present invention refers to all olefins which do not contain a structure represented by $C=CH_2$.

[0012]

The functional group to be introduced into a terminus is preferably hydroxyl, amino, epoxy, carboxyl, ester, ether, amido, silyl and terminal or internal alkenyl groups.

[0013]

The internal olefin of the compound (I) is preferably a cyclic olefin, and 4-vinylcyclohexene and 1,5-cyclooctadiene may be exemplified.

[0014]

The living radical polymerization according to the present invention is preferably carried out in the manner of atom transfer radical polymerization. As a metal complex used as the catalyst is preferably copper, nickel, ruthenium or iron, and copper is particularly preferred.

[0015]

A second aspect of the present invention is a vinyl polymer which has a functional group at a terminus and is obtainable by the present invention. The vinyl polymer is preferably a (meth)acrylate polymer, more preferably an acrylate ester polymer, and particularly preferably a butyl acrylate polymer.

[0016]

In addition, the polymer having a functional group at a terminus obtainable by the present invention also has a characteristic of having a small molecular weight distribution.

[0017]

The polymer having a functional group at a terminus according to the present invention may be used in a curable composition by an appropriate conversion of a functional group such as hydrosilylation and epoxidation, or by addition of a crosslinking agent.

[0018]

[Embodiment of the Invention]

The present invention is a production method of a polymer having a functional group at a terminus by adding a compound (I) having an internal olefin either during or after completion of polymerization in the living radical polymerization.

[0019]

The functional group to be introduced into a terminus is not particularly restricted but preferably hydroxyl, amino, epoxy, carboxyl, ester, ether, amido, silyl and terminal or internal alkenyl groups. Particularly preferred is an alkenyl group.

[0020]

The internal olefin which the compound (I) has is not

particularly restricted but preferably a cyclic olefin.

[0021]

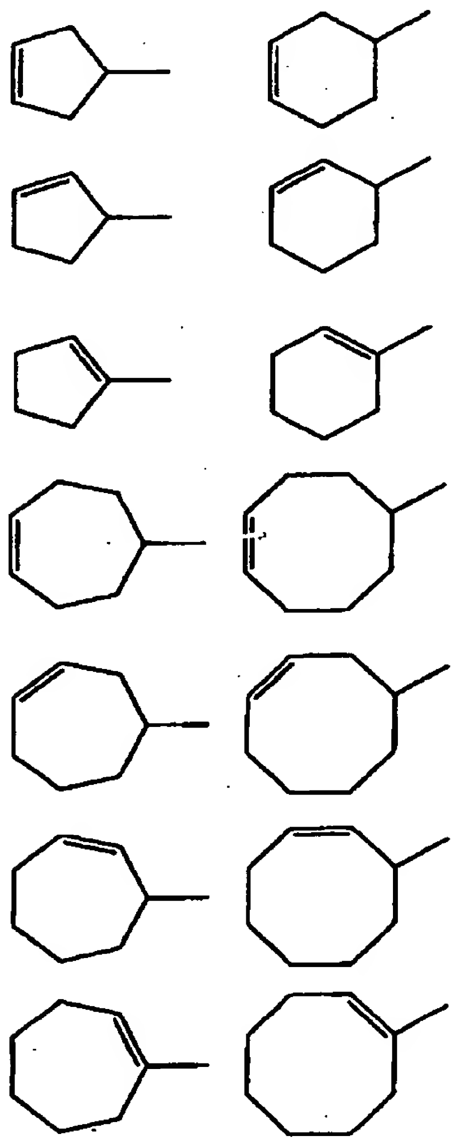
The internal olefin which the compound (I) has is not particularly restricted but includes, among others, the following:

[0022]

CH_3-CH=CH-, R^1-CH=CH-, CH_3-C(R^2)=C(R^3)-, R^1-C(R^2)=C(R^3)-,

[0023]

[Chemical 1]



(In the formulas, R^1, R^2 and R^3 each is an organic group containing 1 to 20 carbon atoms, preferably a hydrocarbon group, and they may be bound to each other to form a ring structure.)

Specific examples of R^1, R^2 and R^3 include, but are not particularly limited to, the following:

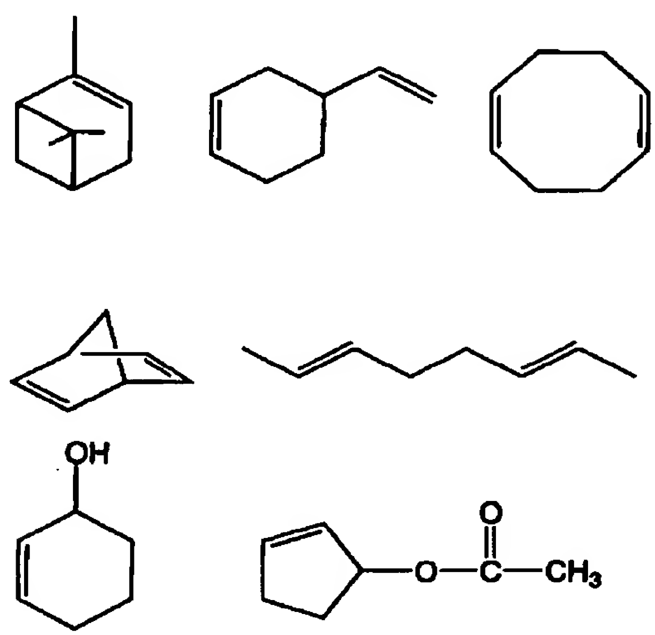
$-(CH_2)_n-CH_3$, $-CH(CH_3)-(CH_2)_n-CH_3$, $-CH(CH_2CH_3)-(CH_2)_n-CH_3$, $-CH(CH_2CH_3)_2$, $-C(CH_3)_2-(CH_2)_n-CH_3$, $-C(CH_3)(CH_2CH_3)-(CH_2)_n-CH_3$, $-C_6H_5$, $-C_6H_5(CH_3)$, $-C_6H_5(CH_3)_2$, $-(CH_2)_n-C_6H_5$, $-(CH_2)_n-C_6H_5(CH_3)$, $-(CH_2)_n-C_6H_5(CH_3)_2$

(n is an integer of not less than 0, and the total number of carbon atoms in each group is not more than 20.)

The compound (I) is not particularly restricted but includes, among others, the following:

[0024]

[Chemical 2]



Among them, preferred are 4-vinylcyclohexene and 1,5-cyclooctadiene.

[0025]

The "living radical polymerization" proceeds at a high rate of polymerization and hardly undergoes any termination

reaction and gives a polymer with a narrow molecular weight distribution (an Mw/Mn value of about 1.1 to 1.5) in spite of its being a mode of that radical polymerization which is regarded as difficult to control because of tendency toward occurrence of termination reactions such as radical-to-radical coupling. It is also possible, in living radical polymerization, to arbitrarily control the molecular weight by adjusting the monomer/initiator charge ratio.

[0026]

The "living radical polymerization" method thus can give a low viscosity polymer with a narrow molecular weight distribution and, in addition, makes it possible to introduce a specific functional group-containing monomer into the polymer mostly at desired sites and, therefore, is more preferred as the production method of the vinyl polymer having a specific functional group mentioned above.

[0027]

While the term "living polymerization", in its narrower sense, means polymerization in which molecular chains grow while the termini thereof always retain their activity, said term generally includes quasi-living polymerization in which terminally inactivated molecules and terminally active molecules grow in a state of equilibrium. The latter definition applies to the living polymerization to be employed in the practice of the present invention.

[0028]

Such "living radical polymerization" has recently been studied actively by various groups of researchers. As examples, there may be mentioned, among others, the use of a cobalt-porphyrin complex as described in the Journal of the American Chemical Society (J. Am. Chem. Soc.), 1994, vol. 116, pages 7943 ff, the use of a radical capping agent such as a nitroxide compound as described in Macromolecules, 1994, vol. 27, pages 7228 ff., and the technique of "atom transfer radical polymerization (ATRP)" which uses an organic halide or the like

as the initiator and a transition metal complex as the catalyst.

[0029]

Among the "living radical polymerization" techniques, the above-mentioned "atom transfer radical polymerization" technique, which uses an organic halide or halosulfonyl compound or the like as the initiator and a transition metal complex as the catalyst for polymerizing vinyl monomers, in addition to the above-mentioned features of "living radical polymerization", gives a polymer terminally having a halogen or the like, which is relatively advantageous to functional group conversion, and the degree of freedom in initiator and catalyst designing and, therefore, is more preferred as the production method of a vinyl polymer having a specific functional group. This atom transfer radical polymerization is described, for example, by Matyjaszewski et al. in the Journal of the American Chemical Society (J. Am. Chem. Soc.), 1995, vol. 117, pages 5614 ff.; Macromolecules, 1995, vol. 28, pages 7901 ff.; Science, 1996, vol. 272, pages 866 ff.; WO 96/30421 and WO 97/18247, and by Sawamoto et al. in Macromolecules, 1995, vol. 28, pages 1721 ff., among others.

[0030]

In the practice of the invention, the atom transfer radical polymerization method is preferred because of ease of control and for other reasons, although there is no particular restriction as to which of the methods or techniques mentioned above is to be employed.

[0031]

First, the technique which uses a radical capping agent such as a nitroxide compound is described. In this polymerization, a nitroxy free radical (=N-O·), which is generally stable, is used as the radical capping agent. While such a compound is not restricted, nitroxy free radicals from cyclic hydroxy amines, such as the 2,2,6,6-substituted-1-piperidinyl oxyradical and 2,2,5,5-substituted-1-pyrrolidinyl oxyradical, are preferred.

Appropriate as the substituents are alkyl groups containing not more than 4 carbon atoms, such as methyl and ethyl groups. Specific nitroxy free radical compounds include, but are not limited to, the 2,2,6,6-tetramethyl-1-piperidinyl oxyradical (TEMPO), 2,2,6,6-tetraethyl-1-piperidinyl oxyradical, 2,2,6,6-tetramethyl-4-oxo-1-piperidinyl oxyradical, 2,2,5,5-tetramethyl-1-pyrrolidinyl oxyradical, 1,1,3,3-tetramethyl-2-isoindolinyl oxyradical and N,N-di-tert-butylamine oxyradical, among others. Such a stable free radical as the galvinoxyl free radical may also be used in lieu of the nitroxy free radical.

[0032]

The above radical capping agent is used in combination with a radical generator. It is presumable that the reaction product from a radical capping agent and a radical generator serves as a polymerization initiator so that the polymerization of an addition-polymerizable monomer(s) proceeds. The mixing ratio of both is not particularly restricted but, appropriately, the radical initiator is used in an amount of 0.1 to 10 moles per mole of the radical capping agent.

[0033]

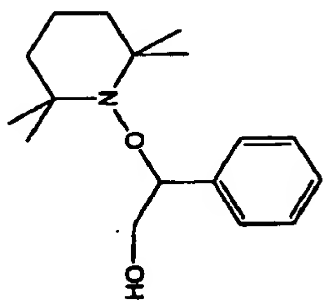
Although various compounds can be used as the radical generator, a peroxide capable of generating a radical under polymerization temperature conditions is preferred. Such peroxide includes, but is not limited to, diacyl peroxides such as benzoyl peroxide and lauroyl peroxide, dialkyl peroxides such as dicumyl peroxide and di-tert-butyl peroxide, peroxydicarbonates such as diisopropyl peroxydicarbonate and bis(4-tert-butylcyclohexyl) peroxydicarbonate, alkyl peresters such as tert-butyl peroxyoctoate and tert-butyl peroxybenzoate, and the like. In particular, benzoyl peroxide is preferred. Further, another radical generator, for example a radical-generating azo compound, such as azobisisobutyronitrile, may also be used in lieu of the peroxide.

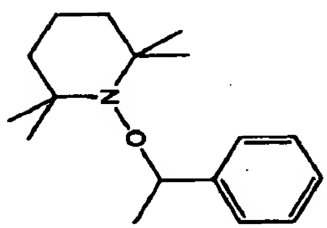
[0034]

As reported in Macromolecules, 1995, vol. 28, page 2993, such alkoxyamine compounds as shown below may be used as the initiator instead of the combined use of a radical capping agent and a radical generator.

[0035]

[Chemical 3]





When an alkoxyamine compound is used as the initiator and it has a hydroxyl or like functional group, as shown above, a polymer terminated in the functional group is obtained. By applying this technique to the method of the invention, star polymers having a functional group at a terminus can be obtained.

[0036]

The polymerization conditions such as the monomer(s) to be used in the polymerization using a radical capping agent e.g. a nitroxide compound as mentioned above, solvent and polymerization temperature are not restricted but may be the same as those used in atom transfer radical polymerization, which is to be mentioned below.

[0037]

The technique of atom transfer radical polymerization, which is more preferred as the technique of living radical polymerization, is now described.

[0038]

In this atom transfer radical polymerization, an organic halide, in particular an organic halide having a highly reactive carbon-halogen bond (e.g. an ester compound having a halogen at the α position, or a compound having a halogen at the benzyl position), or a halosulfonyl compound is preferably used as the initiator. Use is made, as the catalyst, of metal complexes the central metal of which belongs to the group 7, 8, 9, 10 or 11 of the periodic table of the elements. Particularly preferred as the metal species are zero-valent or monovalent copper, divalent ruthenium and divalent iron. As specific examples, there may be mentioned cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous acetate, cuprous perchlorate and the like. When a copper compound is used, a ligand, for example 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof, an alkylamine such as tributylamine or a polyamine such as tetramethylethylenediamine, pentamethyldiethylenetriamine or hexamethyltriethylenetetramine, is added for increasing the catalytic activity. The tristriphenylphosphine complex of divalent ruthenium chloride ($RuCl_2(PPh_3)_3$) is also suited for use as a catalyst. When this catalyst is used, an aluminum compound, such as a trialkoxyaluminum, is added for increasing the activity of the catalyst. Further, the tristriphenylphosphine complex of divalent iron chloride ($FeCl_2(PPh_3)_3$) is also suited as the catalyst.

[0039]

In this polymerization method, an organic halide or halosulfonyl compound is used as the initiator. Specific examples are as follows:

$C_6H_5\text{-}CH_2X$, $C_6H_5\text{-}C(H)(X)CH_3$, $C_6H_5\text{-}C(X)(CH_3)_2$,

(in the above chemical formulas, C_6H_5 represents a phenyl group and X represents a chlorine, bromine or iodine atom):
$R^4-C(H)(X)-CO_2R^5$, $R^4-C(CH_3)(X)-CO_2R^5$, $R^4-C(H)(X)-C(O)R^5$, $R^4-C(CH_3)(X)-C(O)R^5$,
(in the above formulas, R^4 and R^5 each represents a hydrogen atom or a C_{1-20} alkyl group, aryl group or aralkyl group and X represents a chlorine, bromine or iodine atom),
$R^4-C_6H_4-SO_2X$,
(in the above formula, R^4 represents a hydrogen atom or a C_{1-20} alkyl group, aryl group or aralkyl group and X represents a chlorine, bromine or iodine atom), and the like.

[0040]

When an organic halide or halosulfonyl compound having a functional group in addition to one for initiating the polymerization is used, a polymer having functional groups introduced therein at a terminus can readily be obtained. As such functional group, there may be mentioned alkenyl, hydroxyl, epoxy, amino, amide, silyl and like groups.

[0041]

The alkenyl-containing organic halide is not particularly restricted but includes, among others, compounds represented by the general formula 1:

$R^{11}R^{12}C(X)-R^{13}-R^{14}-C(R^6)=CH_2$ (1)

wherein R^6 is a hydrogen atom or a methyl group, R^{11} and R^{12} each is a hydrogen atom or a monovalent C_{1-20} alkyl, aryl or aralkyl group or are bound together at the respective other ends, R^{13} is -C(O)O- (ester group), -C(O)- (keto group) or an o-, m- or p-phenylene group, R^{14} is a direct bond or a divalent organic group containing 1 to 20 carbon atoms and optionally containing one or more ether bonds and X is a chlorine, bromine or iodine atom.

In these compounds, the halogen-bearing carbon atom is bonded to a carbonyl, phenyl or like group and the carbon-halogen bond is thus in an activated state, so that the polymerization can be initiated thereby.

[0042]

As specific examples of R^{11} and R^{12}, there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl and the like. R^{11} and R^{12} may be bound together at the respective other ends to form a ring skeleton and, in such case, $-R^{11}-R^{12}-$ includes, among others, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$ and the like.

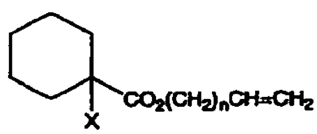
[0043]

As specific examples of the alkenyl-containing organic halide represented by the general formula 1, there may be mentioned the following:

$XCH_2C(O)O(CH_2)_nCH=CH_2$, $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$, $(H_3C)_2C(X)C(O)O(CH_2)_nCH=CH_2$, $CH_3CH_2C(H)(X)C(O)O(CH_2)_nCH=CH_2$,

[0044]

[Chemical 4]



(in each of the above formulas, X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20);

$XCH_2C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,

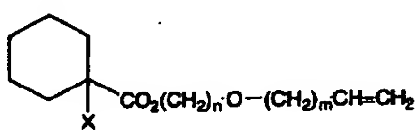
$H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,

$(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,

$CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,

[0045]

[Chemical 5]



(in each of the above formulas, X is a chlorine, bromine or iodine atom, n is an integer of 1 to 20 and m is an integer of 0 to 20);

o, m, p-$XCH_2-C_6H_4-(CH_2)_n-CH=CH_2$, o, m, p-$CH_3C(H)(X)-C_6H_4-(CH_2)_n-CH=CH_2$, o, m, p-$CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_n-CH=CH_2$,

(in each of the above formulas, X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20);

o, m, p-XCH_2-C_6H_4-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2, o, m, p-CH_3C(H)(X)-C_6H_4-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2, o, m, p-CH_3CH_2C(H)(X)-C_6H_4-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2,

(in each of the above formulas, X is a chlorine, bromine or iodine atom, n is an integer of 1 to 20 and m is an integer of 0 to 20);

o, m, p-XCH_2-C_6H_4-O-$(CH_2)_n$-CH=CH_2, o, m, p-CH_3C(H)(X)-C_6H_4-O-$(CH_2)_n$-CH=CH_2, o, m, p-CH_3CH_2C(H)(X)-C_6H_4-O-$(CH_2)_n$-CH=CH_2,

(in each of the above formulas, X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20);

o, m, p-XCH_2-C_6H_4-O-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2, o, m, p-CH_3C(H)(X)-C_6H_4-O-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2, o, m, p-CH_3CH_2C(H)(X)-C_6H_4-O-$(CH_2)_n$-O-$(CH_2)_m$-CH=CH_2,

(in each of the above formulas, X is a chlorine, bromine or iodine atom, n is an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general formula 2:

$$H_2C=C(R^6)-R^{14}-C(R^{11})(X)-R^{15}-R^{12} \qquad (2)$$

wherein R^6, R^{11}, R^{12}, R^{14} and X are as defined above and R^{15} represents a direct bond, -C(O)O- (ester group), -C(O)- (keto group) or an o-, m- or p-phenylene group.

R^{14} is a direct bond or a divalent organic group containing 1 to 20 carbon atoms (optionally containing one or more ether bonds). When it is a direct bond, the vinyl group is bonded to the halogen-bearing carbon atom, hence the compound is an allyl halide compound. In this case, it is not always necessary for the compound to have a C(O)O or phenylene group as R^{15}, since the carbon-halogen bond is activated by the neighboring vinyl group. Thus, it may be a direct bond. When R^{14} is not a direct bond, a C(O)O group, a C(O) group and a phenylene group are

preferred as R^{15} so that the carbon-halogen bond may be activated.

[0046]

As specific examples of the compound of general formula 2, there may be mentioned, among others, the following:
$CH_2=CHCH_2X$, $CH_2=C(CH_3)CH_2X$, $CH_2=CHC(H)(X)CH_3$, $CH_2=C(CH_3)C(H)(X)CH_3$, $CH_2=CHC(X)(CH_3)_2$, $CH_2=CHC(H)(X)C_2H_5$, $CH_2=CHC(H)(X)CH(CH_3)_2$, $CH_2=CHC(H)(X)C_6H_5$, $CH_2=CHC(H)(X)CH_2C_6H_5$, $CH_2=CHCH_2C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_2C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_3C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_8C(H)(X)-CO_2R$, $CH_2=CHCH_2C(H)(X)-C_6H_5$, $CH_2=CH(CH_2)_2C(H)(X)-C_6H_5$, $CH_2=CH(CH_2)_3C(H)(X)-C_6H_5$,
(in each of the above formulas, X is a chlorine, bromine or iodine atom and R is a C_{1-20} alkyl, aryl or aralkyl group).

[0047]

As specific examples of the alkenyl-containing halosulfonyl compound, there may be mentioned, among others, the following:
o-, m-, p-$CH_2=CH-(CH_2)_n-C_6H_4-SO_2X$,
o-, m-, p-$CH_2=CH-(CH_2)_n-O-C_6H_4-SO_2X$,
(in each of the above formulas, X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20).

[0048]

As regards the alkenyl-containing initiator, it is possible for the olefin of that initiator as well to react with the polymer terminus. Therefore, care should be taken in selecting the polymerization reactions and the reaction conditions for the olefin compound to be added. As a specific example, there may be mentioned the addition of the olefin compound at an early stage of polymerization.

[0049]

The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, compounds having a structure represented by the general formula 3:
$R^{11}R^{12}C(X)-R^{13}-R^{14}-C(H)(R^6)CH_2-[Si(R^{16})_{2-b}(Y)_bO]_m-Si(R^{17})_{3-a}(Y)_a$

(3)

wherein R^6, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, a, b, m, X and Y are as defined above.

As specific examples of the compound of general formula 3, there may be mentioned, among others, the following: $XCH_2C(O)O(CH_2)_nSi(OCH_3)_3$, $CH_3C(H)(X)C(O)O(CH_2)_nSi(OCH_3)_3$, $(CH_3)_2C(X)C(O)O(CH_2)_nSi(OCH_3)_3$, $XCH_2C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$, $CH_3C(H)(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$, $(CH_3)_2C(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$, (in each of the above formulas, X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20); $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$, $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$, $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$, $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$, (in each of the above formulas, X is a chlorine, bromine or iodine atom, n is an integer of 1 to 20 and m is an integer of 0 to 20); o, m, p-XCH_2-C_6H_4-$(CH_2)_2Si(OCH_3)_3$, o, m, p-$CH_3C(H)(X)$-C_6H_4-$(CH_2)_2Si(OCH_3)_3$, o, m, p-$CH_3CH_2C(H)(X)$-C_6H_4-$(CH_2)_2Si(OCH_3)_3$, o, m, p-XCH_2-C_6H_4-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3C(H)(X)$-C_6H_4-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3CH_2C(H)(X)$-C_6H_4-$(CH_2)_3Si(OCH_3)_3$, o, m, p-XCH_2-C_6H_4-$(CH_2)_2$-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3C(H)(X)$-C_6H_4-$(CH_2)_2$-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3CH_2C(H)(X)$-C_6H_4-$(CH_2)_2$-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-XCH_2-C_6H_4-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3C(H)(X)$-C_6H_4-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3CH_2C(H)(X)$-C_6H_4-O-$(CH_2)_3Si(OCH_3)_3$, o, m, p-XCH_2-C_6H_4-O-$(CH_2)_2$-O-$(CH_2)_3Si(OCH_3)_3$, o, m,

p-$CH_3C(H)(X)-C_6H_4-O-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$, o, m, p-$CH_3CH_2C(H)(X)-C_6H_4-O-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$,
(in each of the above formulas, X is a chlorine, bromine or iodine atom).

[0050]

The crosslinking silyl-containing organic halide further includes compounds having a structure represented by the general formula 4:

$$(R^{17})_{3-a}(Y)_aSi-[OSi(R^{16})_{2-b}(Y)_b]_m-CH_2-C(H)(R^6)-R^{14}-C(R^{11})(X)-R^{15}-R^{12} \quad (4)$$

wherein R^6, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, a, b, m, X and Y are as defined above.

As specific examples of such compound, there may be mentioned, among others, the following:

$(CH_3O)_3SiCH_2CH_2C(H)(X)C_6H_5$, $(CH_3O)_2(CH_3)SiCH_2CH_2C(H)(X)C_6H_5$,
$(CH_3O)_3Si(CH_2)_2C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_3C(H)(X)-CO_2R$,
$(CH_3O)_2Si(CH_2)_4C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_3C(H)(X)-CO_2R$,
$(CH_3O)_3Si(CH_2)_4C(H)(X)-CO_2R$, $(CH_3O)_3(CH_3)Si(CH_2)_4C(H)(X)-CO_2R$,
$(CH_3O)_2Si(CH_2)_9C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_9C(H)(X)-CO_2R$,
$(CH_3O)_3Si(CH_2)_3C(H)(X)-C_6H_5$, $(CH_3O)_2(CH_3)Si(CH_2)_3C(H)(X)-C_6H_5$,
$(CH_3O)_3Si(CH_2)_4C(H)(X)-C_6H_5$, $(CH_3O)_2(CH_3)Si(CH_2)_4C(H)(X)-C_6H_5$,
(in each of the above formulas, X is a chlorine, bromine or iodine atom and R is a C_{1-20} alkyl, aryl or aralkyl group).

[0051]

The hydroxyl-containing organic halide or halosulfonyl compound is not particularly restricted but includes, among others, the following:

$HO-(CH_2)_n-OC(O)C(H)(R)(X)$

(in the above formula, X is a chlorine, bromine or iodine atom, R is a hydrogen atom or a C_{1-20} alkyl, aryl or aralkyl group and n is an integer of 1 to 20).

The amino-containing organic halide or halosulfonyl compound is not particularly restricted but includes, among others, the following:

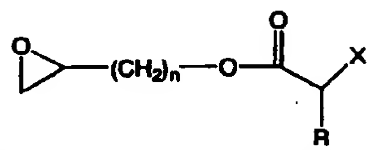
$H_2N-(CH_2)_n-OC(O)C(H)(R)(X)$

(in the above formula, X is a chlorine, bromine or iodine atom, R is a hydrogen atom or a C_{1-20} alkyl, aryl or aralkyl group and n is an integer of 1 to 20).

The epoxy-containing organic halide or halosulfonyl compound is not particularly restricted but includes, among others, the following:

[0052]

[Chemical 6]

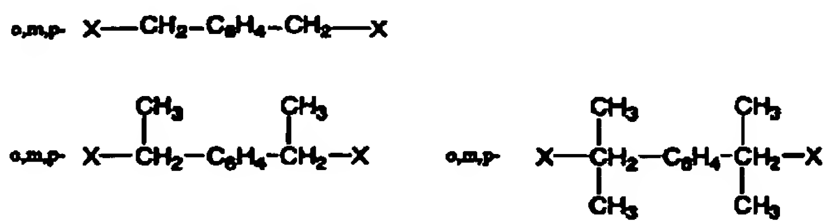


(in the above formula, X is a chlorine, bromine or iodine atom, R is a hydrogen atom or a C_{1-20} alkyl, aryl or aralkyl group and n is an integer of 1 to 20).

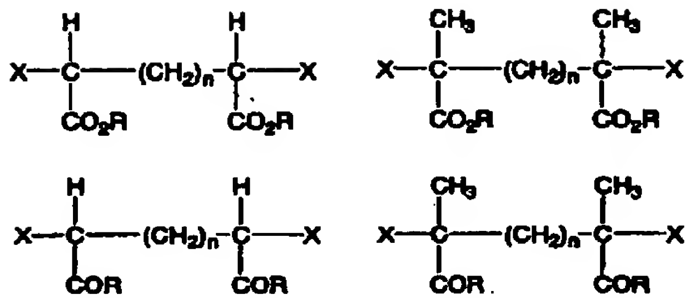
For obtaining a polymer having two or more olefin-terminated structure per molecule of the present invention, an organic halide or halosulfonyl compound having two or more initiation sites is used as the initiator. As specific examples, there may be mentioned the following:

[0053]

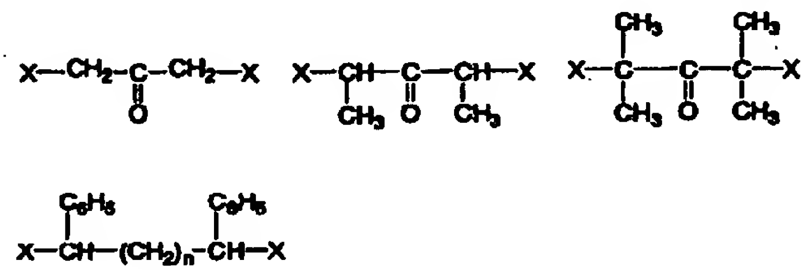
[Chemical 7]



(wherein C_6H_4 represents a phenylene group and X is a chlorine, bromine or iodine atom);



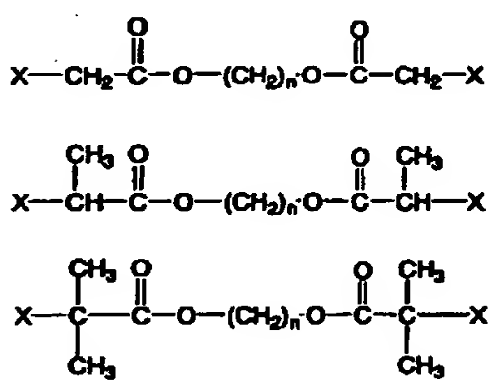
(wherein R is a C_{1-20} alkyl, aryl or aralkyl group, n is an integer of 0 to 20 and X is a chlorine, bromine or iodine atom);



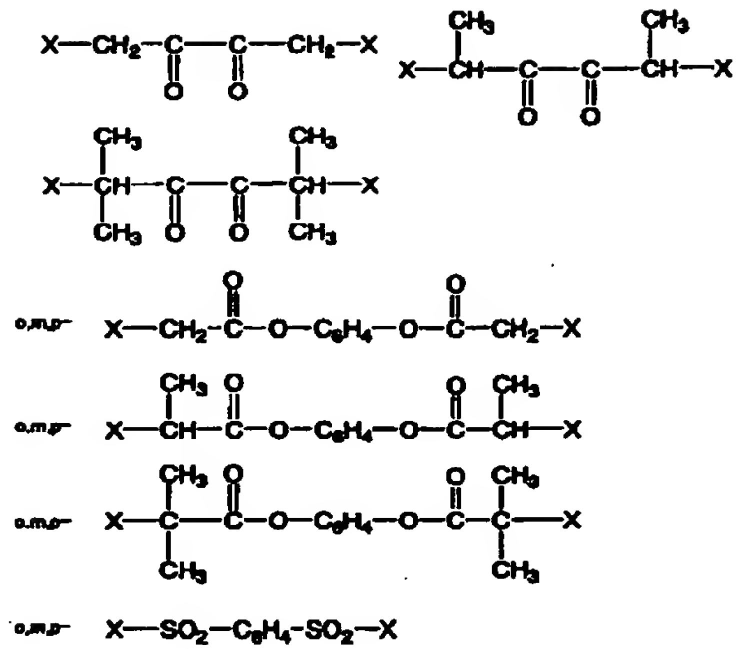
(wherein X is a chlorine, bromine or iodine atom and n is an integer of 0 to 20);

[0054]

[Chemical 8]



(wherein n is an integer of 0 to 20 and X is a chlorine, bromine or iodine atom);



(wherein X is a chlorine, bromine or iodine atom).

[0055]

The polymerizable olefin monomer to be used in this polymerization is not particularly restricted but includes various species. Since the polymerization system indicated herein is a living polymerization system, it is also possible to produce block copolymers by successively adding polymerizable monomers. As examples, there may be mentioned (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate,

glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ-(methacryloyloxy)propyltrimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate, 2-perfluorohexadecylethyl (meth)acrylate and like (meth)acrylic monomers; styrene, vinyltoluene, α-methylstyrene, chlorostyrene, styrenesulfonic acid and salts thereof, and like styrenic monomers; perfluoroethylene, perfluoropropylene, vinylidene fluoride and like fluorine-containing vinyl monomers; vinyltrimethoxysilane, vinyltriethoxysilane and like silicon-containing vinyl monomers; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide, cylcohexylmaleimide and like maleimide monomers; acrylonitrile, methacrylonitrile and like nitrile group-containing vinyl monomers; acrylamide, methacrylamide and like amide group-containing vinyl monomers; vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, vinyl cinnamate and like vinyl esters; ethylene, propylene and like alkenes; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride and allyl alcohol, among others. These may be used singly or a plurality of such monomers may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of products, among others. Acrylic ester monomers are more preferred from the viewpoint

of high reactivity in functional group introduction reactions and/or low glass transition point, for instance, and butyl acrylate is particularly preferred.

[0056]

The polymerization can be carried without using any solvent or in various solvents. These are not particularly restricted but include, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture.

[0057]

The polymerization can be carried out within the range of room temperature to 200°C, preferably 50 to 150°C.

[0058]

When the compound (I), which has an internal olefin group, is added during or at the end point of such polymerization, approximately one molecule of the compound adds to each terminus and, as a result, the functional group which the compound (I), which has an internal olefin group, has is introduced into the molecular terminus. The "end point" of polymerization means the time point at which the conversion of the monomer(s) is preferably not less than 80%, more preferably not less than 90%, still more preferably not less than 95%, most preferably not less than 99%.

[0059]

When a compound having an amino, hydroxyl or carboxyl group is reacted with a polymer terminus, the compound may be

reacted as it is, but in some cases, those groups may possibly affect the polymer terminus or catalyst. On that occasion, such compounds can be used in a form protected with a protective group. As appropriate protective groups, there may be mentioned acetyl, silyl, alkoxy and like groups.

[0060]

The amount of the compound to be added which is used for introducing these functional groups is not particularly restricted. Since the reactivity of the alkenyl group of such compound is not very high, it is preferred to increase the addition amount thereof for increasing the rate of reaction. On the other hand, for cost reduction purposes, that amount is desirably as close as possible to the equimolar amount relative to the growing terminus. It is thus necessary to optimize that amount according to circumstances.

[0061]

The amount, to be added, of a compound having two or more olefins, inclusive of an internal olefin, for introducing an alkenyl group terminally, is preferably in excess relative to the growing polymer terminus. An equimolar amount or a smaller amount may possibly allow both the two olefins to react, resulting in coupling of polymerization termini. In the case of a compound whose two olefins are equal in reactivity, the probability of occurrence of such coupling is determined statistically depending on the amount added in excess. Therefore, the amount is preferably not less than 1.5 times, more preferably not less than 3 times, still more preferably not less than 5 times.

[0062]

The second aspect of the invention is directed to a polymer having a functional group at a terminus which is obtainable by the production method of the present invention.

[0063]

As for the polymer having a functional group at a terminus which is obtainable by the method of the present invention, the

terminal group is introduced by addition of an olefin to a growing terminus in living radical polymerization of a vinyl polymer. Therefore, the polymer is characterized in that approximately one terminal group is bonded to one terminus of the polymer by means of direct carbon-carbon bonding alone without being mediated by a hetero atom.

[0064]

The number of terminal groups contained in a molecule of the polymer is not particularly restricted but, when the polymer is used in a curable composition, for instance, two or more are preferably contained therein.

[0065]

The polymer of the invention has a molecular weight distribution, namely weight average molecular weight-to-number average molecular weight ratio as determined by gel permeation chromatography, of preferably not more than 1.8, more preferably not more than 1.6, most preferably not more than 1.3.

[0066]

The polymer of the invention preferably has a number average molecular weight within the range of 500 to 100,000, more preferably 3,000 to 40,000. When the molecular weight is less than 500, the vinyl polymer will hardly manifest those characteristics which are intrinsic in vinyl polymers. When it is higher than 100,000, handling becomes difficult.

[0067]

The polymer produced in accordance with the present invention is utilized as such, namely the functional group introduced is utilized as such, or after conversion of that group to some other functional group by conducting a further conversion reaction. More specifically, an alkenyl group can be converted to a crosslinking silyl group by the hydrosilylation reaction using a crosslinking silyl-containing hydrosilane compound. Suited for use as the alkenyl-terminated vinyl polymer are all of those obtainable

by the method already illustrated hereinabove.

[0068]

The hydrosilane compound is not particularly restricted but, as typical example, there may be mentioned compounds represented by the general formula 5:

$H-[Si(R^{19})_{2-b}(Y)_bO]_m-Si(R^{20})_{3-a}(Y)_a$ (5)

wherein R^{19} and R^{20} each is an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms or a triorganosiloxy group represented by $(R')_3SiO-$ (in which R' is a hydrocarbon group containing 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when two or more R^{19} or R^{20} exist, they may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when two or more Y groups exist, they may be the same or different; a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19 provided that the relation $a + mb \geq 1$ is to be satisfied.

The above hydrolyzable group represented by Y is not particularly restricted but any of those known in the art may be used. Specifically, there may be mentioned hydrogen, halogen atoms, and alkoxy, acyloxy, ketoximato, amino, amido, acid amide, aminoxy, mercapto, alkenyloxy and like groups. From the mild hydrolyzability and easy handling viewpoint, alkoxy groups are particularly preferred. One to three groups selected from among the hydrolyzable and hydroxyl groups can be bonded to a silicon atom and the sum a + mb, namely the total number of hydrolyzable groups, is preferably within the range of 1 to 5. When the reactive silyl group contains two or more hydrolyzable and/or hydroxyl groups bonded thereto, these may be the same or different. The number of silicon atoms constituting the crosslinking silicon compound may be one or two or more. In the case of silicon atoms linked by siloxane bonding, the number may be up to about 20.

[0069]

As specific examples of R^{19} and R^{20}, there may be mentioned,

among others, alkyl groups such as methyl and ethyl, cycloalkyl groups such as cyclohexyl, aryl groups such as phenyl, aralkyl groups such as benzyl, and triorganosilyl groups represented by $(R')_3SiO-$ in which R' is methyl or phenyl, for instance.

[0070]

Among such hydrosilane compounds, crosslinking group-containing hydrosilane compounds represented by the general formula 6:

$H-Si(R^{20})_{3-a}(Y)_a$ (6)

wherein R^{20}, Y and a are as defined above, are preferred from the ready availability viewpoint. As specific examples of the crosslinking group-containing hydrosilane compound represented by the general formula 5 or 6, there may be mentioned, among others:

$HSiCl_3$, $HSi(CH_3)Cl_2$, $HSi(CH_3)_2Cl$, $HSi(OCH_3)_3$, $HSi(CH_3)(OCH_3)_2$, $HSi(CH_3)_2OCH_3$, $HSi(OC_2H_5)_3$, $HSi(CH_3)(OC_2H_5)_2$, $HSi(CH_3)_2OC_2H_5$, $HSi(OC_3H_7)_3$, $HSi(C_2H_5)(OCH_3)_2$, $HSi(C_2H_5)_2OCH_3$, $HSi(C_6H_5)(OCH_3)_2$, $HSi(C_6H_5)_2(OCH_3)$, $HSi(CH_3)(OC(O)CH_3)_2$, $HSi(CH_3)_2O-[Si(CH_3)_2O]_2-Si(CH_3)(OCH_3)_2$, $HSi(CH_3)[O-N=C(CH_3)_2]_2$ (in the above chemical formulas, C_6H_5 represents a phenyl group).

[0071]

In causing such a crosslinking silyl-containing hydrosilane compound to add to an alkenyl-terminated vinyl polymer, a hydrosilylation catalyst is used. As such hydrosilylation catalyst, there may be mentioned radical initiators such as organic peroxides and azo compounds as well as transition metal catalysts.

[0072]

The radical initiator is not particularly restricted but may be any of various compounds. As examples, there may be mentioned dialkyl peroxides such as di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)-3-hexyne, dicumyl peroxide, tert-butyl cumyl peroxide and

α,α'-bis(tert-butylperoxy)isopropylbenzene, diacyl peroxides such as benzoyl peroxide, p-chlorobenzoyl peroxide, m-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide and lauroyl peroxide, peresters such as tert-butyl perbenzoate, peroxydicarbonates such as diisopropyl peroxydicarbonate and di-2-ethylhexyl peroxydicarbonate, and peroxyketals such as 1,1-di(tert-butylperoxy)cyclohexane and 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, among others.

[0073]

As the transition metal catalyst, there may be mentioned, for example, simple substance platinum, solid platinum dispersed on a support such as alumina, silica or carbon black, chloroplatinic acid, complexes of chloroplatinic acid with alcohols, aldehydes, ketones or the like, platinum-olefin complexes and platinum(0)-divinyltetramethyldisiloxane complex. As examples of the catalyst other than platinum compounds, there may be mentioned $RhCl(PPh_3)_3$, $RhCl_3$, $RuCl_3$, $IrCl_3$, $FeCl_3$, $AlCl_3$, $PdCl_2\cdot H_2O$, $NiCl_2$, $TiCl_4$, etc. These catalyst may be used singly or two or more of them may be used combinedly. The amount of the catalyst is not particularly restricted but recommendably is within the range of 10^{-1} to 10^{-8} mole, preferably within the range of 10^{-3} to 10^{-6} mole, per mole of the alkenyl group of the component (A). When it is less than 10^{-8} mole, the curing may not proceed to a sufficient extent. Since the hydrosilylation catalyst is expensive, it is recommendable that it be not used in an amount exceeding 10^{-1} mole.

[0074]

The hydroxyl group at a terminus is converted to an alkenyl group by the condensation reaction with allyl chloride or allyl bromide using an alkaline compound. It can also be converted to an epoxy group by the same reaction using epichlorohydrin.

Furthermore, the hydroxyl or amino group at a terminus

can be converted to a crosslinking silyl group by reacting with a crosslinking silyl group-containing compound having a functional group reacting with a hydroxyl or amino group. As the functional group capable of reacting with a hydroxyl or amino group, there may be mentioned, among others, halogens, and carboxylic acid halide, carboxylic acid, isocyanato and like groups. The isocyanato group is preferred, however, in view of ready availability of compounds, mild reaction conditions in reacting with the hydroxyl group and resistance to crosslinking silyl group decomposition.

[0075]

Such crosslinking silyl-containing isocyanate compound is not particularly restricted but may be any of those known in the art. As specific examples, there may be mentioned, among others, the following:

$(CH_3O)_3Si-(CH_2)_n-NCO$, $(CH_3O)_2(CH_3)Si-(CH_2)_n-NCO$,
$(C_2H_5O)_3Si-(CH_2)_n-NCO$, $(C_2H_5O)_2(CH_3)Si-(CH_2)_n-NCO$,
$(i-C_3H_7O)_3Si-(CH_2)_n-NCO$, $(i-C_3H_7O)_2(CH_3)Si-(CH_2)_n-NCO$,
$(CH_3O)_3Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
$(CH_3O)_2(CH_3)Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
$(C_2H_5O)_3Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
$(C_2H_5O)_2(CH_3)Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
$(i-C_3H_7O)_3Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
$(i-C_3H_7O)_2(CH_3)Si-(CH_2)_n-NH-(CH_2)_m-NCO$,
(in the above formulas, n and m each is an integer of 1 to 20).

[0076]

The reaction between the hydroxyl-terminated (meth)acrylic polymer and the crosslinking silyl-containing isocyanate compound can be carried out without using any solvent or in any of various solvents at a reaction temperature of 0°C to 100°C, preferably 20°C to 50°C. On that occasion, any of the tin catalysts or tertiary amine catalysts already mentioned hereinbefore can be used for promoting the reaction between the hydroxyl and isocyanate groups.

[0077]

The third aspect of the invention is directed to a curable composition which comprises the polymer having a functional group at a terminus according to the present invention and in which one of various crosslinking reactions is utilized.

[0078]

The alkenyl-terminated polymer can be used in formulating a curable composition comprising (A) the alkenyl-containing polymer and (B) a hydrosilyl group-containing compound.

The component (A), alkenyl-terminated vinyl polymer may be used singly or a mixture of two or more thereof may be used. The molecular weight of the component (A) is not particularly restricted but preferably within the range of 500 to 100,000, more preferably 3,000 to 40,000. When it is less than 500, those characteristics which are intrinsic in vinyl polymers will be hardly manifested and, when it is above 100,000, a very high viscosity or a decreased solubility will result, rendering the handling difficult.

[0079]

The component (B), namely hydrosilyl-containing compound, is not particularly restricted but may be any of various ones. Thus, use may be made of linear polysiloxanes represented by the general formula 7 or 8:

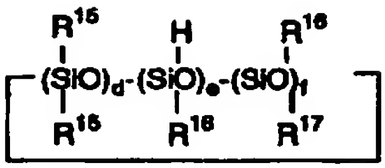
$$R^{16}{}_3SiO-[Si(R^{15})_2O]_a-[Si(H)(R^{16})O]_b-[Si(R^{16})(R^{17})O]_c-SiR^{15}{}_3 \quad (7)$$

$$HR^{15}{}_2SiO-[Si(R^{15})_2O]_a-[Si(H)(R^{16})O]_b-[Si(R^{16})(R^{17})O]_c-SiR^{15}{}_2H \quad (8)$$

wherein R^{15} and R^{16} each represents an alkyl group containing 1 to 6 carbon atoms or a phenyl group, R^{17} represents an alkyl group containing 1 to 10 carbon atoms or an aralkyl group containing 7 to 10 carbon atoms, a represents an integer $0 \leq a \leq 100$, b an integer $2 \leq b \leq 100$ and c an integer $0 \leq c \leq 100$); and cyclic siloxanes represented by the general formula 9:

[0080]

[Chemical 9]



(9)

wherein R^{15} and R^{16} each represents an alkyl group containing 1 to 6 carbon atoms or a phenyl group, R^{17} represents an alkyl group containing 1 to 10 carbon atoms or an aralkyl group containing 7 to 10 carbon atoms, d represents an integer $0 \leq d \leq 8$, e an integer $2 \leq e \leq 10$ and f an integer $0 \leq f \leq 8$ on condition that $3 \leq d + e + f \leq 10$.

[0081]

These may be used singly or two or more of them may be used in admixture. Among these siloxanes, those phenyl-containing linear siloxanes represented by the general formula 10 or 11 given below and phenyl-containing cyclic siloxanes represented by the general formula 12 or 13 given below are preferred in view of the compatibility with the vinyl polymers.

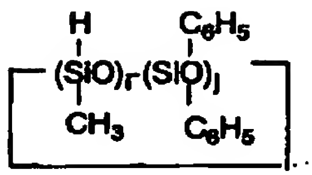
$$(CH_3)_3SiO-[Si(H)(CH_3)O]_g-[Si(C_6H_5)_2O]_h-Si(CH_3)_3 \quad (10)$$

$$(CH_3)_3SiO-[Si(H)(CH_3)O]_g-[Si(CH_3)\{CH_2C(H)(R^{18})C_6H_5\}O]_h-Si(CH_3)_3 \quad (11)$$

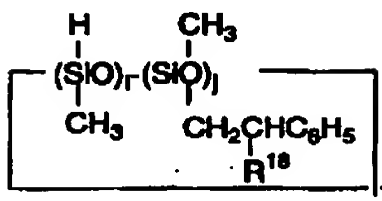
(in the formulas, R^{18} represents a hydrogen atom or a methyl group, g represents an integer $2 \leq g \leq 100$ and h an integer $0 \leq h \leq 100$ and C_6H_5 represents a phenyl group);

[0082]

[Chemical 10]



(12)



(13)

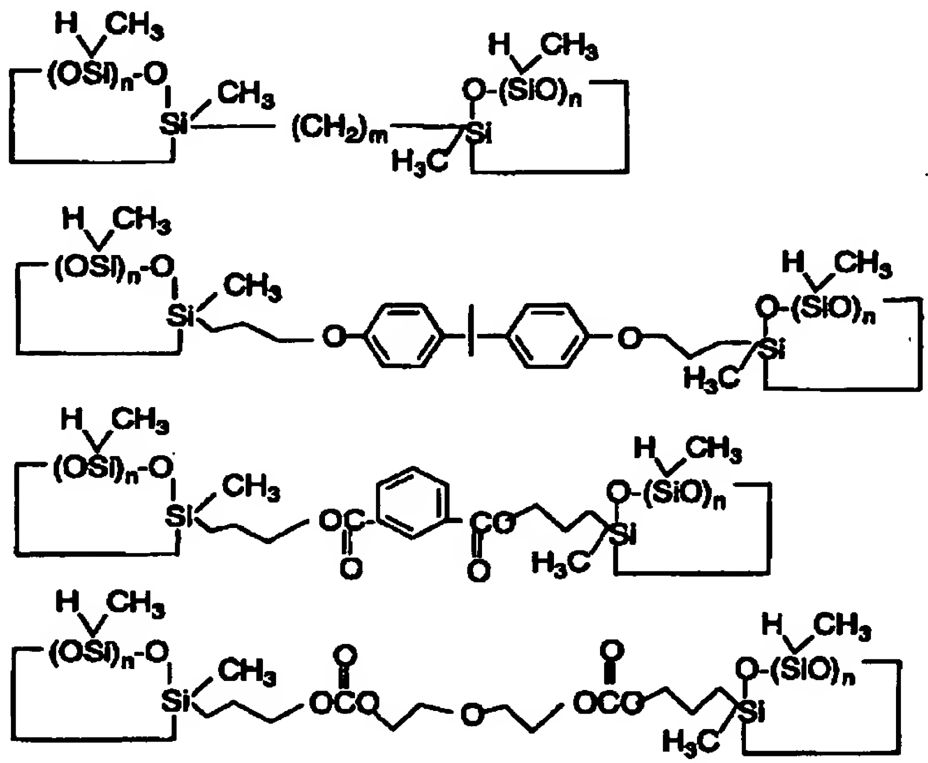
(in the formulas, R^{18} represents a hydrogen atom or a methyl group, i represents an integer $2 \leq i \leq 10$ and j an integer $0 \leq j \leq 8$ on condition that $3 \leq i + j \leq 10$ and C_6H_5 represents a phenyl group).

Also useful as the component (B), namely curing agent having at least two hydrosilyl groups, are compounds obtainable by subjecting a hydrosilyl-containing compound represented by one of the general formulas 7 to 13 to addition reaction with a low-molecular compound having two alkenyl groups per molecule so that the hydrosilyl-containing group may partly remain even after the reaction. Useful as the compound having two or more alkenyl groups per molecule are various compounds. As examples, there may be mentioned hydrocarbon compounds such as 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene, ether compounds such as O,O'-diallylbisphenol A and 3,3'-diallylbisphenol A, ester compounds such as diallyl phthalate, diallyl isophthalate, triallyl trimellitate and tetraallyl pyromellitate, and carbonate compounds such as diethylene glycol diallyl carbonate.

[0083]

The above compounds can be obtained by slowly adding dropwise an alkenyl-containing compound as mentioned above to an excessive amount of a hydrosilyl-containing compound in the presence of a hydrosilylation catalyst. Preferred among such

compounds in view of ready availability of starting materials, ease of removal of the siloxane used in excess and, further, compatibility with the component (A) polymer are the following:
[0084]
[Chemical 11]



(n being an integer of 2 to 4 and m being an integer of 5 to 10).

The polymer (A) and curing agent (B) can be blended in an arbitrary ratio. From the curability viewpoint, however, the alkenyl-to-hydrosilyl mole ratio is preferably within the range of 5 to 0.2, more preferably 2.5 to 0.4. When the mole ratio is not less than 5, the curing becomes insufficient, hence only sticky cured products low in strength are obtained. When it is less than 0.2, a large amount of the active hydrosilyl group remains in the cured products even after curing, causing formation of cracks and voids; any uniform and strong cured products cannot be obtained.

[0085]

The curing reaction between the polymer (A) and curing agent (B) proceeds upon blending the two components and heating. For allowing the reaction to proceed more rapidly, a hydrosilylation catalyst is added. As such hydrosilylation catalyst, any of those various ones already mentioned hereinabove may be used.

[0086]

The polymer having a crosslinking silyl group at a terminus can be used in a curable composition which comprises the polymer as the main component.

[0087]

Upon coming into contact with water or moisture, the vinyl polymer having a crosslinking silyl group at a terminus is cured in a three-dimensional manner by the curing reaction. Since the rate of hydrolysis depends on the temperature, humidity and hydrolyzable group species, an appropriate hydrolyzable group should be selected according to the use conditions.

[0088]

For promoting the curing reaction, a condensation catalyst may be added. As the condensation catalyst, use may be made of one or two of known silanol condensation catalysts, as necessary, for example titanate esters such as tetrabutyl titanate and tetrapropyl titanate; organotin compounds such as dibutyltin dilaurate, dibutyltin maleate, dibutyltin diacetate, stannous octoate and stannous naphtheneate; lead octylate; amine compounds such as butylamine, octylamine, dibutylamine, monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, oleylamine, octylamine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylenediamine, triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethylamino-methyl)phenol, morpholine, N-methylmorpholine and 1,3-diazabicyclo[5.4.6]undecene-7, or salts of these amine compounds with carboxylic acids; low-molecular polyamide

resins obtained from an excess polyamine and a polybasic acid; reaction products from an excess polyamine and an epoxy compound; amino-containing silane coupling agents such as γ-aminopropyltrimethoxysilane and N-(β-aminoethyl)aminopropylmethyldimethoxysilane; and the like. They are preferably used in an amount of 0.01 to 10% by weight relative to the crosslinking silyl-terminated vinyl polymer. When an alkoxy group is used as the hydrolyzable silyl group Y, this polymer, if used alone, shows a slow rate of curing, hence the use of a curing catalyst is preferred.

[0089]

When the crosslinking silyl-terminated vinyl polymer, which is the main component, is admixed with a condensation catalyst as necessary and allowed to be cured, uniform cured products can be obtained. While the curing conditions are not particularly restricted, the curing reaction is generally effected at 0 to 100°C, preferably 10 to 50°C, for about 1 hour to 1 week. Although the properties of the cured products depend on the main chain skeleton and molecular weight of the polymer, a wide varieties of products, from rubber-like ones to resin-like ones, can be produced.

[0090]

When the crosslinking silyl-terminated vinyl polymer, which is the main component, is admixed with a condensation catalyst as necessary and allowed to be cured, uniform cured products can be obtained. While the curing conditions are not particularly restricted, the curing reaction is generally effected at 0 to 100°C, preferably 10 to 50°C, for about 1 hour to 1 week. Although the properties of the cured products depend on the main chain skeleton and molecular weight of the polymer, a wide varieties of products, from rubber-like ones to resin-like ones, can be produced.

[0091]

The polymer having a hydroxyl group at a terminus obtainable by the above-mentioned various methods can be used

in a curable composition which comprises that polymer as the main component.

[0092]

This curable composition comprises, as essential components thereof, the following two components: (A) the hydroxyl-terminated vinyl polymer and (B) a compound having two or more functional groups capable of reacting with the hydroxyl group.

[0093]

The hydroxyl-terminated vinyl polymer, namely component (A), may be used singly or two or more thereof may be used in mixture. The molecular weight thereof is not particularly restricted but preferably is within the range of 500 to 100,000. When it is less than 500, those characteristics which are intrinsic in vinyl polymers will be hardly manifested and, when it is above 100,000, a very high viscosity or a decreased solubility will result, rendering the handling difficult in certain instances.

[0094]

The compound having two or more functional groups capable of reacting with a hydroxyl group of component (B) is not particularly restricted but includes, among others, polyisocyanate compounds having two or more isocyanato groups per molecule, aminoplast resins such as methylolmelamines and alkyl-etherified derivatives thereof or low condensation products therefrom, polyfunctional carboxylic acids and halides thereof.

[0095]

Useful as the polyisocyanates having two or more isocyanato groups per molecule are those known in the art, for example isocyanate compounds such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethanediisocyanate, hexamethylene diisocyanate, xylylene diisocyanate, metaxylylene diisocyanate, 1,5-naphthalenediisocyanate, hydrogenated diphenylmethanediisocyanate, hydrogenated

tolylene diisocyanate, hydrogenated xylylene diisocyanate, isophoronediisocyanate,Ipposha Yushi's B-45 and like triisocyanates, biuret polyisocyanate compounds such as Sumidur N (product of Sumitomo Bayer Urethane), isocyanurate ring-containing polyisocyanates such as Desmodur IL and HL (products of Bayer A.-G.) and Coronate EH (product of Nippon Polyurethane Industry), adduct polyisocyanate compounds such as Sumidur L (product of Sumitomo Bayer Urethane), and adduct polyisocyanate compounds such as Coronate HL (product of Nippon Polyurethane Industry). Blocked isocyanates may also be used. These may be used singly or two or more of them may be used.

[0096]

The mixing ratio between the hydroxyl-terminated polymer and the compound having two or more isocyanato groups is not particularly restricted but, for example, the ratio between the isocyanato groups and the hydroxyl groups of the hydroxyl-terminated vinyl polymer (NCO/OH (mole ratio)) is preferably 0.5 to 3.0, more preferably 0.8 to 2.0.

[0097]

For promoting the curing reaction between the hydroxyl-terminated vinyl polymer, which is a composition of the present invention, and the compound having two or more isocyanato groups, a catalyst known in the art, such as an organotin compound or a tertiary amine, may be added according to need.

[0098]

As specific examples of the organotin compound, there may be mentioned stannous octoate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin mercaptides, dibutyltin thiocarboxylates, dibutyltin dimaleates, dioctyltin thiocarboxylates and the like. As the tertiary amine catalyst, there may be mentioned triethylamine, N,N-dimethylcyclohexylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropane-1,3-diamine,

N,N,N',N'-tetramethylhexane-1,6-diamine, N,N,N',N",N"-pentamethyldiethylenetriamine, N,N,N',N",N"-pentamethyldipropylenetriamine, tetramethyl-guanidine, triethylenediamine, N,N'-dimethylpiperazine, N-methylmorpholine, 1,2-dimethylimidazole, dimethylaminoethanol, dimethylaminoethoxyethanol, N,N,N'-trimethylaminoethylethanolamine, N-methyl-N'-(2-hydroxyethyl)piperazine, N-(2-hydroxyethyl)morpholine, bis(2-dimethylaminoethyl) ether, ethylene glycol bis(3-dimethylaminopropyl) ether and the like.

[0099]

The aminoplast resin to be used in the curable composition of the invention is not particularly restricted but includes addition products from melamine and formaldehyde (methylol compounds), low condensates from melamine and formaldehyde, and alkyl-etherifired modifications thereof, as well as urea resins and the like. These may be used singly or two or more of them may be used in combination. For promoting the curing reaction between the hydroxyl-terminated (meth)acrylic polymer and the aminoplast resin, a known catalyst such as p-toluenesulfonic acid or benzenesulfonic acid may be used.

[0100]

The compound having two or more carboxyl groups per molecule, which is to be used in the curable composition of the invention is not particularly restricted but includes, among others, polyfunctional carboxylic acids and anhydrides thereof, such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, phthalic acid, phthalic anhydride, terephthalic acid, trimellitic acid, pyromellitic acid, maleic acid, maleic anhydride, fumaric acid and itaconic acid as well as halides of these. These may be used singly or two or more of them may be used in combination.

[0101]

By mixing up the two components (A) and (B) according to

the invention, if necessary together with a curing catalyst, it is possible to obtain uniform cured products excellent in degree of depth curing. Although the curing conditions are not particularly restricted, the curing is generally carried out at 0°C to 100°C, preferably 20°C to 80°C.

[0102]

While the properties of the cured product depend on the main chain skeleton and molecular weight of the (A) component polymer and (B) component curing agent, a wide variety of products can be produced, from rubber-like to resin-like.

[0103]

The polymer having an epoxy group at a terminus can be used in a curable composition which comprises (A) the epoxy-terminated polymer and (B) a curing agent. Usable as the curing agent (B) are various ones, for example aliphatic amines, aromatic amines, acid anhydrides, urea, melamine and phenol resins.

[0104]

Specific uses of the cured products obtainable from the compositions of the invention as mentioned above include sealing materials, adhesives, pressure-sensitive adhesives, elastic adhesives, coatings, powder coatings, foamed articles, potting materials for electric and electronic use, films, molding materials and artificial marble, among others.

[0105]

[Examples]

In the following, several specific examples of this invention are described. It is to be noted, however, that the following examples are by no means limitative of the scope of this invention.

(Example 1)

A 200-mL glass reactor was charged, under nitrogen, with butyl acrylate (100.0 mL, 89.4 g, 697.5 mmol), cuprous bromide (375 mg, 2.62 mmol), diethyl 2,5-dibromoadipate (3.14 g, 8.72 mmol) and acetonitrile (10 mL). The mixture was heated at 70°C

with stirring, and the polymerization was initiated by adding pentamethyldiethylenetriamine (0.18 mL, 151 mg, 0.87 mmol).

[0106]

After 125 minutes, 4-vinylcyclohexene (22.67 mL, 18.86 g, 174.4 mmol) was added and pentamethyldiethylenetriamine was added. At this time point, the conversion of butyl acrylate was about 90%. Stirring with heating was continued at 70°C for 280 minutes. The mixture was treated with activated alumina and the excess 4-vinylcyclohexene (boiling point °C) was distilled off by heating under reduced pressure. It was confirmed by ^{1}H-NMR spectrometry that the alkenyl group had been introduced into the polymer.

(Example 2)

The polymerization was carried out in the same manner as in Example 1 and 1,5-cyclooctadiene was added in lieu of 4-vinylcyclohexene. After treatment in the same manner, it was confirmed by ^{1}H-NMR spectrometry that an alkenyl group had been introduced into the polymer.

(Example 3)

The alkenyl-terminated polybutyl acrylate polymer synthesized in the same manner as in Examples 1 and 2 was reacted with methyldichlorosilane using a platinum catalyst. The hydrosilylation reaction proceeded and the silyl group was introduced terminally into the polymer.

(Example 4)

Water and a tin catalyst were added to the crosslinking silyl-terminated polybutyl acrylate polymer synthesized in the same manner as in Example 3, whereupon a rubber-like cured product was obtained.

[0107]

[Effect of the Invention]

The vinyl polymer of the invention which has a functional group at a terminus is stable since the terminal group is bonded to the main chain through carbon-carbon bonding and, further, since the structure is well controlled, namely each terminus

has only one olefin, the polymer is useful in utilizing the same in a curable composition, for instance. According to the production method of the invention, it is possible to produce a polymer having various functional groups at a terminus as mentioned above easily from various vinyl polymers by adding the compound indicated in the present invention which has an internal olefin and various functional groups to the polymerization system.

[Document Name] Abstract

[Abstract]

[Subject] To provide a polymer of radically polymerizable olefin monomers which has various functional groups at a terminus, a production method thereof, and a composition using those polymers, by using an internal olefin compound.

[Means for Solving] To obtain said polymer by adding a compound containing internal olefins such as 4-vinylcyclohexene and 1,5-cyclohexadiene to a polymerization system during or after completion of polymerization in living radical polymerization.